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| <p>(54) Title: A METHOD FOR PREPARING IMPREGNATED CELLULOSE FIBERS HAVING A LOW WATER RETENTION AND PRODUCTS HEREBY OBTAINED</p> <p>(57) Abstract</p> <p>A method for preparing cellulose fibers having a low water retention value which method comprises applying a tetraalkoxysilane or an oligomer thereof to cellulose fibers with a water content of 1-10% by weight, in particular 2-7% by weight, or which, simultaneously with or subsequent to the application, are imparted a water content in the range of 1-10% by weight, in particular 2-7% by weight. The prepared fibers may be hydrophobic or hydrophilic and are especially useful as reinforcing fibers in a composite material together with cement or other inorganic matrixes.</p> <p style="text-align: center;">BEST AVAILABLE COPY</p> | | |

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A method for preparing impregnated cellulose fibres having a low water retention and products hereby obtained."

5 The present invention concerns impregnated cellulose fibres in which the free hydroxy groups of the cellulose have been treated with a silane, thereby imparting the cellulose fibres a low water retention value, and to a method for preparing such impregnated cellulose fibres.

There have been a number of attempts to prepare cellulose fibres with a low water retention value, primarily for use as reinforcing fibres in various matrices such as cement or plastics, in order to replace such fibrous materials as glass fibre or asbestos. There is a particular
10 need for a replacement for asbestos since asbestos fibres have been found to be the cause of such conditions as silicosis and lung cancer.

One particular group of impregnating agents previously used are the metal oxide acylates. It is possible with metal oxide acylates to prepare cellulose fibres that have a very low water retention value, i.e.
15 less 0.5%. The use of metal oxide acylates as an impregnating agent normally requires that the fibres have been dried to a water content of at least below 2%, and preferably in the range of about 0.01%, because the metal oxide acylates react with water forming insoluble metal soaps that prevent or impede the metal oxide acylates from
20 reacting with the hydroxy groups of the cellulose. Also, due to the long hydrocarbon chains of the metal oxide acylates, the resulting fibres may be so hydrophobic that it requires special means to disperse the fibres in for example an aqueous cement gel.

In order to improve the dispersibility of metaloxideacylate-impregnated
25 fibres it has been attempted to treat metal oxide acylate impregnated fibres with a silane (cf. Applicants International Patent Application No. PCT/DK82/00052, Publication No. WO 82/04271).

It has now surprisingly been found that cellulose fibres having a low water retention value may be prepared by reacting a silane directly
30 with the cellulose fibre without the need for any substantial drying of the water present in the fibre (a cellulose fibre in equilibrium generally contains about 7% by weight of water).



Accordingly, the present invention provides a method for preparing impregnated cellulose fibres having a low water retention value, comprising applying a tetraalkoxy silane or an oligomer thereof to cellulose fibres which have a water content in the range of 1-10% by weight, in particular 2-7% by weight, or which, simultaneously with or subsequent to the application, are imparted a water content in the range of 1-10% by weight, in particular 2-7% by weight.

As used herein, the term "alkoxy" denotes an alkoxy group of 1-4 carbon atoms such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy and tert.butoxy, preferably ethoxy. The term "oligomer" means that the silane comprises a siloxane chain of preferably 2-10 silicon atoms.

Contrary to the aforementioned use of metal oxide acylates, where drying is essential, it is not necessary to perform any substantial drying of the fibres since a certain amount of water present is necessary for impregnating fibres according to the method of the invention. This is due to the fact that the reaction involves a hydrolysis of the alkoxy silane whereby water is consumed. However, it is desirable to carry out a minor amount of drying, e.g. if the fibres have been subjected to direct contact with water or subjected to a high relative humidity, the fibres may be dried gently such as by irradiation with infrared light or by vacuum-drying.

Such silanes have previously been used primarily as a corrosion protection agent for steel, in particular when admixed with zinc dust. It is also known that for example tetraethoxy silane (which may also be regarded as a tetraethyl ester of silicic acid) may be converted into silicic acid esters of higher alcohols by a transesterification-type reaction. One surprising feature of the present invention is that it is possible for a tetraalkoxy silane to react directly with cellulose; the explanation probably resides in the fact that cellulose may also be regarded as a polyhydric alcohol.

Besides allowing reaction with the hydroxy groups of the cellulose, the hydrolysis of the alkoxy silane also generates a number of silyl-



- hydroxy groups about which groups it is known that two such groups situated on two separate silicon atoms have a great affinity for performing a dehydration reaction and forming a silicon-oxygen-silicon link. Thus, the method of the invention also makes it possible to
- 5 prepare impregnated cellulose fibres in which the individual cellulose chains (consisting of glucose units) and/or the individual microfibrils within the cellulose fibres are cross-linked with one another by the silicon-oxygen-silicon link. This reaction will greatly improve the stability and low water absorptivity of the fibres. Furthermore,
- 10 hydroxysilane groups on the surface of the fibres which have not reacted with another identical group, will tend to create a hydrophilic milieu on the surface of the fibre. Such a hydrophilicity is especially useful if the fibre is to be utilized in an aqueous environment such as in a cement matrix.
- 15 The reaction rate of the hydrolysis of the alkoxysilane and hence the reaction rate of the transesterification reaction depends on the pH of the reaction environment in that the hydrolysis proceeds very slowly at neutral or near-neutral pH but is accelerated if the environment is acidic or basic. In view of the fact that cellulose fibres generally
- 20 have a pH value in the range of 5-7 it is preferable to apply an acidic or basic catalyst to the fibres prior to, during, or subsequent to the application of the silane. The catalyst may be applied in the form of a solution, either aqueous or organic, or it may be present in a solid state. Basic catalysts are preferred since acids may tend to
- 25 break down the cellulose itself. Examples of acidic catalysts include hydrochloric acid, ammonium dihydrogenphosphate, polyboric acid, and aluminium sulphate. Examples of basic catalysts include ammonia or an amine, but the catalyst may also be for example a basic polymer, such as an ion exchange resin, deposited on the fibres. The catalysts
- 30 may optionally have been deposited on the fibres during the manufacture thereof.
- A particularly useful type of amine is an aminoalkyltrialkylsiloxy silane, in which the aminoalkyl moiety may have 1-4 carbon atoms, in particular 3 carbon atoms. This type of compound has the advantage that
- 35 it seems to react in concert with the alkoxy silane thereby creating a



basic environment situated directly on the fibre. Such a basic environment aids in completing the hydrolysis of the alkoxy silane and further causes the fibre to have a cationic reaction which will render the fibre highly hydrophilic and further increases the compatibility with e.g. a basic cement gel.

An especially preferred method according to the invention is one in which the fibres are treated with a tetraalkyloxy silane or an oligomer thereof and an aminoalkyltrialkyloxy silane in ratio of about 100:0.1-100:10, in particular in a ratio of about 100:1-100:5. This is because a too high concentration of the catalysing aminoalkyltrialkyloxy silane may result in a too swift reaction causing poor penetration of the impregnating agent. The two compounds may be applied as a mixture or separately, in the latter case either the alkoxy silane first and the aminoalkyl trialkyloxy silane second or vice versa, or the two compounds may be applied simultaneously but without being in admixture initially, for example by spraying the two compounds and allowing the two sprays to mix.

The particularly preferred type of alkyloxy silane oligomer is a mixture of oligomers of up to 10 silicon atoms optionally in admixture with monomer.

When applied to cellulose fibres having the above mentioned water content, excess of the alkoxy silane will be hydrolyzed by the water present forming silicic acid which will, however, not prevent the silane from reacting with the hydroxy groups of the cellulose. Since the actual impregnation of the hydroxy groups of the cellulose does not require a very large amount of silane and since silanes of the above mentioned type are fairly inexpensive it is possible to apply an excess of silane in order to dispose of the water present in the fibres. In view of the fact that one gram of water may consume approximately 3-5 grams or more of silane (depending on the molecular weight) it is preferable to apply the silane to the fibres in an amount in the range of 1-40% by weight of the fibres in particular 1-20% by weight, such as 3-20% by weight.



Fibres treated with the above-mentioned large excess of the alkoxy silane will, since unreacted silane may also react with silane already fixed on the fibre, have the advantage of being non-flammable or at any rate only combustible with great difficulty. Consequently, such
5 fibres are particularly useful for use as an insulating material in e.g. building wall cavities.

If the amount of catalyst present is low, or if no catalyst is applied, the silane may take a long time to react with the fibres. Consequently, it is possible to accelerate the process by treating the fibres with
10 heat and in an atmosphere of high relative humidity after the application of the silane, or by treating the fibres with water optionally containing an acid or a base and optionally while heating. As examples of acids and bases may be mentioned for example hydrochloric acid and ammonia. The treatment may be performed for a period of up
15 to 24 hours.

In order to facilitate the dosing and application, the silane may be applied when the fibres are in the form of a web of paper or cellulose pulp such as sulphate or sulphite pulp, hardwood and softwood pulp, cereal cellulose pulp, including straw cellulose pulp. Preferred types
20 of fibres are for example waste fibres or virgin fibres. The cellulose fibres, to which the silane is applied, may also be in the form of wood, fiber board, wood chip board, or plywood (both untreated or treated with CCA or CCP agents), wood chips or shavings, saw dust, wood wool, synthetic or regenerated cellulose fibres, sisal, acacie, or
25 coconut fibres, or cotton.

If the cellulose fibres are impregnated in the form of a web or roll, the fibres may be subjected to a defibration treatment subsequent to or simultaneously with the impregnation as the defibration treatment will aid the distribution of the impregnating agent throughout each
30 fiber. The defibration treatment is preferably performed in a hammer mill or a disc defibrator.

The silane and/or the catalyst may be applied by various means such as direct application with a brush, immersion into the impregnating agent followed by removal of excess by means of squeezing pressure,



or it may preferably be applied in the form of droplets under reduced pressure, in particular a vacuum, since this procedure facilitates an accurate dosage and ensures a better distribution of the impregnating agent. The pressure during the spraying may be in the range of
5 1-700 millibar, preferably in the range of 1-100 millibar, in particular 1-50 millibar, especially 1-10 millibar, since the low pressure favours the formation of very small droplets.

In order to ensure a good penetration of the silane and at the same time ensure a reasonably rapid reaction between the silane and the
10 cellulose once the penetration is complete, it is preferable to apply the catalyst, in particular the amino compound, to the fibres after the silane compound and immediately prior to defibration in the hammer mill or disc defibrator. Thereby the silane, which has a low viscosity (in the region of $1-5 \text{ mm}^2/\text{s}$) even at room temperature will have
15 penetrated well into the fibres before being activated by the catalyzing amino compound. A good penetration ensures that the fibres are impregnated under and into the small fibrilles (the number and size of which determines the SR° of the fibre) as well so that the fibres will remain non-water absorbing, even following grinding with
20 water to increase the SR° of the fibre.

The penetration may also be improved by corona treating the cellulose fibres prior to the application of the impregnating agent. The corona treatment will lower the surface tension of the fibres, thus ensuring an even better penetration.

25 It is also interesting to apply a silicon-titaniumalkoxide condensed oligomer to the fibres in an amount of about 1-10% calculated on the fibres together with a catalyst as described above, in particular an aminoalkyltrialkyloxysilane with the above described ratio between the condensed oligomer and the catalyzing silane. The silicon-titaniumalkoxide oligomer may in particular be applied prior to the catalyzing
30 silane or in admixture with the catalyzing silane. The silicon-titaniumalkoxide oligomer is available as such or may be prepared for immediate use by reacting a tetraalkoxy silane with a titanium tetraalkoxide in a predetermined ratio, usually a molar ratio of approximately
35 1:2.



The fibres may also be treated in situ when they are already embedded in an inorganic matrix, in particular cement, gypsum or calcium silicate. The matrix may be in form of for example building panels, such as wall plates or roof plates, and the application may be performed either by applying with a brush or spraying the impregnating agent on the plates in an amount of between 1 and 30%, preferably 5-25%, in particular 10-20%, such as 15% by weight of the entire plate. This procedure causes the plate not to swell when subjected to water, which is an indication that the fibres have been rendered non-water absorbant, since the water-absorbing qualities of untreated fibres causes for example cement plates reinforced with untreated fibres to swell when wetted.

The invention also concerns cellulose fibres obtainable by the process described above, that is, cellulose fibres in which the free hydroxy groups are substituted with a monomeric or oligomeric alkoxysilyl group. The number of substituted hydroxy groups is preferably above 75%, especially above 85%, in particular above 90% of the total number of free hydroxy groups in the cellulose. The free hydroxy groups are preferably also substituted with an aminoalkyldialkoxysilyl group.

The fibres, whether hydrophobic or hydrophilic, prepared according to the method of the invention may, apart from the uses mentioned above, be useful for the following uses: Reinforcing material in various thermoplastic or thermosetting polymers such as epoxy polyesters, phenol resins, polyolefins etc., polymer foams, gas or light concrete, as backing in e.g. non-woven fabrics, wallpaper, floor paper, tar paper and in any other situation where a non-absorbing fibre is needed.



Details on products used in the following examples are as follows:

- 5 TES 40 Mixture of ethyl silicic acid esters (ethyloxysiloxanes) having 1-9 silicon atoms per molecule, average formula $\text{Si}(\text{OC}_2\text{H}_5)_{2.33}\text{O}_{0.835}$. From Wacker Chemie.
- Silane A-1100 A silane coupling agent, consisting of γ -aminopropyltriethoxysilane, from Union Carbide.
- TES 28 Tetraethyloxysilane monomer. From Wacker Chemie, Federal Republic of Germany.

- 10 In the examples which follow, the treating agents or combination of treating agents listed was applied to a cellulose web under reduced atmospheric pressure with immediate subsequent defibration in a hammer mill. The treatments were performed in a treatment plant comprising supply rollers, a corona treatment unit, vacuum chamber
- 15 fitted with application jets for the impregnating in treating agents, and a hammer mill, of the type as described in Applicants' co-pending Danish Application filed on the same day as the present application, and entitled "Fremgangsmåde til imprægnering af et fibrøst materiale" (Method for impregnating a fibrous material).



EXAMPLE 1

| | | |
|----|-------------------------------------|---|
| | Paper type | 400 g paper from unbleached sulphate cellulose waste |
| 5 | Impregnating agent | TES 40 + Silane A-1100 mixed in a ratio of 96:4 |
| | Room temperature | 20°C |
| | Paper speed | 14 m/min |
| | Air pressure at application site | 775 millibar |
| 10 | Amount of fibres treated | 330 kg |
| | Dosage of polymer applied | 82 g per kg of paper |

15 The fibres had completed the reaction after about 10 days, after which it was not possible to extract unreacted silane. The fibres felt dry and were very hydrophilic, in that they were readily wettable by water. The fibres reacted cationic with a zeta-potential of approximately +30. The water retention value was below 0.50%, and the fibres dispersed easily in cement giving a uniform distribution in the matrix.

20 Using the same conditions as in Example 1 regarding fibre type, room temperature, paper speed, and air pressure the treated fibres listed in the following table were prepared using the listed amounts of the particular impregnating agent.



TABLE

| | Impregnating agent | Amount applied in grammes per 1 kg fibres | | | | | | | |
|----|-------------------------------|---|-----|-----|----|-----|-----|----|-----|
| | | Example Nos. | | | | | | | |
| | | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 5 | TES 28 | 51 | 150 | 350 | | | | | |
| | TES 40 | | | | 70 | 120 | 397 | | |
| | TES 28 + A-1100 ratio 96:4 | | | | | | | 82 | |
| 10 | TES 40 + A-1100 ratio 99:1 | | | | | | | | 407 |

TABLE cont.

| | Impregnating agent | Amount applied in grammes per 1 kg fibres | | | | | | | |
|----|-------------------------------|---|-----|-----|-----|----|-----|-----|--|
| | | Example Nos. | | | | | | | |
| | | 10 | 11 | 12 | 13 | 14 | 15 | 16 | |
| 15 | TES 40 + A-1100 ratio 98:2 | 380 | | | | | | | |
| 20 | ratio 97:3 | | 422 | | | | 120 | | |
| | ratio 96:4 | | | 420 | | | | 120 | |
| | ratio 95:5 | | | | 390 | 80 | | | |

25 In the Examples 2-7 it took several months of reaction time at room temperature and normal ambient humidity before it was not possible to extract impregnating agent from the fibres. The resulting fibres were strongly hydrophobic. After treatment by immersion with an ammonia solution or an aqueous solution of A-1100 for 3-24 hours, the fibres gradually became hydrophilic.



The fibres of the examples 8-10 became strongly hydrophilic after a reaction time of 3-5 months. The water retention value was less than 0.50%.

5 The fibres of the Examples 11-16 all completed their reaction within 6-20 days, after which time nothing could be extracted from the fibres. The fibres felt dry and reacted hydrophilic and cationic with a zeta-potential of from +27 to +57. The water retention value was below 0.50% and the fibres were easily dispersible in cement similar to the fibres of Example 1.

10 EXAMPLE 17

Bleached virgin sulphate fibres with an SR° of 16 were treated with 35% by weight of a mixture of TES 40 and Silane A-1100 in a ratio of 96:4. The fibre became hydrophilic after approximately 36 hours.

EXAMPLE 18

15 Cement plates containing the fibres prepared according to Example 1 were prepared using 4,5% by weight (calculated on the amount of cement) of fibres in a mixture of cement and water in a ratio of 0.58:1. The plates were compressed to a density of 1.890 kg/m^3 . After a maturing period of 7 days the hydroexpansion was found to be 0.13% (as opposed to 0.26% with untreated fibres), and the tensile
20 strength of the plates was found to be 15.76 MPa in wet condition and 17.83 MPa in dry condition, which amounts to a reduction in the tensile strenght of only 11.6% going from dry to wet condition. This surpasses excellently the 20% difference in tensile strength that is
25 normally the minimum requirement for cement composite materials.

EXAMPLE 19

Kraft paper (lining paper made from unbleached pine sulphate pulp) was first treated with a 25% ammonia solution which was sprayed on the paper in amounts between 10 and 20%, and was subsequently
30 treated with TES 40 in an amount of 10-20%. The treatment resulted



in a very dimension stable kraft paper which was first hydrophobic, but was made hydrophilic by accelerating the reaction through heating at 80-90°C for 5 minutes.

EXAMPLE 20

- 5 A mixture was prepared of 284 g titaniumtetraisopropoxide (TPT), 300g TES 40, and 1,6 g Silane A-1100. Kraft paper was treated with 10% by weight of the mixture, and the paper was defibrated. After 24 hours cement plates were cast using 9 g fibres, 191 g Portland cement and 300 g water. The mixture was mixed thoroughly in a mixer
10 for 3 minutes, and excess water was sucked off. The result was a smooth uniform fibre cement plate with a good distribution of the fibres. The water/cement ratio was 0.24, compared with 0.16 for a pure Portland cement/water mixture and 0.40 for a fibre cement comprising untreated cellulose fibres indicating that the fibres only
15 absorbed very little or no water.

EXAMPLE 21

- A cement plate with a thickness of 8 mm, reinforced with 4.5% untreated virgin sulphate fibres, and a water/cement ratio of above 30 was impregnated by spraying with 15% by weight TES 40 (calculated
20 on the weight of the plate). The impregnated plate did not absorb any water and acted water-repellent.



CLAIMS

1. A method for preparing impregnated cellulose fibres having a low water retention value, comprising applying a tetraalkoxysilane or an oligomer thereof to cellulose fibres which have a water content in the range of 1-10% by weight, in particular 2-7% by weight, or which, simultaneously with or subsequent to the application, are imparted a water content in the range of 1-10% by weight, in particular 2-7% by weight.
2. A method according to claim 1 in which an acid or basic catalyst is also applied on the fibres prior to, during, or subsequent to the application of the silane.
3. A method according to claim 2 in which the basic catalyst is ammonia or an amine.
4. A method according to claim 3 in which the amine is an aminoalkyl-trialkylloxysilane.
5. A method according to claims 1-4 in which the fibres are treated with a tetraalkyloxy silane or an oligomer thereof and an aminoalkyl trialkyloxy silane in a ratio from about 100:0.1-100:10.
6. A method according to claim 5 in which the tetraalkyloxy silane and the aminoalkyl trialkyloxy silane are applied in a ratio of about 100:1-100:5.
7. A method according to any of the preceding claims wherein the oligomer is a mixture of oligomers of up to 10 silicon atoms optionally in admixture with monomer.
8. A method according to any of the preceding claims in which the amount of silane applied is in the range of 1-40% by weight.
9. A method according to claim 8 in which the amount of silane applied is in the range of 1-20% by weight.



10. A method according to claim 8 in which the amount of silane applied is in the range of 3-20% by weight.
11. A method according to any of the preceding claims wherein the fibres, after the application of the silane, are treated with heat and
5 in an atmosphere of high relative humidity.
12. A method according to any of claims 1-10 in which the treated fibres are thereafter treated with water optionally containing an acid or a base and optionally during heating.
13. A method according to claim 11 and 12 in which the treatment is
10 performed for a period of up to 24 hours.
14. A method according to any of the preceding claims wherein the fibres to which the silane is applied are in the form of a web of paper or cellulose pulp.
15. A method according to any of claims 1-13 in which the cellulose
15 fibres are in the form of waste fibres or virgin fibres.
16. A method according to any of claims 1-13 in which the cellulose fibres are in the form of wood or wood chips or shavings, saw dust wood wool, synthetic or regenerated cellulose fibres, fibre board, wood chip board, plywood, sulphate or sulphite pulp, hardwood and
20 softwood pulp, cereal cellulose pulp, including straw cellulose pulp, sisal, acacie, or coconut fibres, or cotton.
17. A method according to any of the preceding claims wherein the cellulose fibres are in the form of a web or roll and are subjected to a defibration treatment subsequent to or simultaneously with the
25 impregnation.
18. A method according to claim 17 in which the defibration is performed in a hammer mill or a disc defibrator.



19. A method according to claim 18 in which the silane is applied in the hammer mill or defibrator.
20. A method according to claim 17 in which the silane and/or the catalyst is applied in the form of droplets under reduced pressure, in particular vacuum.
21. A method according to any of the preceding claims wherein the amino compound is applied after the silane compound and immediately prior to defibration in the hammer mill or disc defibrator.
22. A method according to any of the preceding claims wherein the cellulose fibres are corona treated prior to the application.
23. A method according to any of the preceding claims wherein a silicon-titaniumalkoxide condensed oligomer is also applied on the fibres.
24. A method according to claim 23 in which the silicon-titaniumalkoxide oligomer is applied in an amount of about 1-10%, calculated on the fibres.
25. A method according to claims 23 and 24 in which the silicon-titaniumalkoxide oligomer is applied prior to the silane or in admixture with the silane.
26. A method according to any of claims 1-10 in which the fibres are treated in situ when embedded in an inorganic matrix.
27. A method according to claim 26 in which the inorganic matrix is cement, gypsum, or calcium silicate.
28. Cellulose fibres in which the free hydroxy groups are substituted with a monomeric or oligomeric alkoxysilyl group.
29. Fibres according to claim 28 in which the free hydroxy groups are also substituted with an aminoalkyl dialkoxysilyl group.



INTERNATIONAL SEARCH REPORT

International Application No PCT/DK84/00047

| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹ According to International Patent Classification (IPC) or to both National Classification and IPC ³ <div style="margin-top: 5px;">D 21 H 3/62</div> | | | | | | | | |
|--|---|-------------------------------------|---|---|--|---|---|-----------------|
| II. FIELDS SEARCHED <div style="text-align: center; margin-top: 5px;">Minimum Documentation Searched ⁴</div> <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <tr> <th style="width: 25%;">Classification System</th> <th style="width: 75%;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px;">IPC 3 US C1</td> <td style="padding: 5px;">D 21 H 3/02; D 21 H 3/62; D 06 M 13/00 <u>162:182-184</u>; <u>428:447</u></td> </tr> </table> <div style="text-align: center; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵</div> <div style="margin-top: 10px;">SE, NO, DK, FI classes as above</div> | | | Classification System | Classification Symbols | IPC 3 US C1 | D 21 H 3/02; D 21 H 3/62; D 06 M 13/00 <u>162:182-184</u> ; <u>428:447</u> | | |
| Classification System | Classification Symbols | | | | | | | |
| IPC 3 US C1 | D 21 H 3/02; D 21 H 3/62; D 06 M 13/00 <u>162:182-184</u> ; <u>428:447</u> | | | | | | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <tr> <th style="width: 10%;">Category ⁶</th> <th style="width: 60%;">Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷</th> <th style="width: 30%;">Relevant to Claim No. ¹⁸</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 10px;">X</td> <td style="padding: 10px;"> US, A, 4 386 134 (JOSEF PÜHRINGER) 31 May 1983 & WO, 80/02249 EP, 0033316 CA, 1136358 AU, 59881/80 </td> <td style="text-align: center; vertical-align: top; padding: 10px;"> 1-4, 8-10 16 </td> </tr> </table> | | | Category ⁶ | Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No. ¹⁸ | X | US, A, 4 386 134 (JOSEF PÜHRINGER) 31 May 1983 & WO, 80/02249 EP, 0033316 CA, 1136358 AU, 59881/80 | 1-4, 8-10 16 |
| Category ⁶ | Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No. ¹⁸ | | | | | | |
| X | US, A, 4 386 134 (JOSEF PÜHRINGER) 31 May 1983 & WO, 80/02249 EP, 0033316 CA, 1136358 AU, 59881/80 | 1-4, 8-10 16 | | | | | | |
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